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PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-176012

(43)Date of publication of application : 30.06.1998

(51)Int.Cl.

C08F 8/04
C08F212/08
C08F232/06
// C09D125/10
C09D145/00
C09J125/10
C09J145/00

(21)Application number : 08-353359

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(22)Date of filing : 17.12.1996

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(54) HYDROGENATED COPOLYMER HAVING BLOCKING RESISTANCE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a hydrogenated copolymer excellent in hue and blocking resistance, useful as a base for an adhesive, by controlling hydrogenation ratio to adjust a bromine number to a fixed range.

SOLUTION: This hydrogenated copolymer comprises a hydrogenated resin of a copolymer of a cyclopentadiene-based unit and a monovinyl-substituted aromatic hydrocarbon unit and has a bromine number in a range of 10-25g/100g. The resin, is preferably a hydrogenated resin of a copolymer of a cyclopentadiene unit and/or a dicyclopentadiene unit and a styrene unit, and the copolymerization reaction is carried out, for example, at 180-320° C for 1-8 hours under 0-30kg/cm2 G.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

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CLAIMS

[Claim(s)]

[Claim 1] The blocking resistance copolymer hydrogenation object which consists of hydrogenation resin of the copolymer of a cyclopentadiene system unit and a mono-vinyl permutation aromatic hydrocarbon unit, and has the bromine number of the range of 10-25g/100g.

[Claim 2] The blocking resistance copolymer hydrogenation object according to claim 1 whose hydrogenation resin is hydrogenation resin of the copolymer of a cyclopentadiene unit and/or a dicyclopentadiene unit, and a styrene unit.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is excellent in blocking resistance, and relates to a blocking resistance copolymer hydrogenation object useful as a binder for toners etc. as base materials, such as adhesives, a binder, and a coating.

[0002]

[Description of the Prior Art] The hydrogenation resin of a cyclopentadiene system monomer and the copolymer of mono-vinyl permutation aromatic hydrocarbon is known, and it is useful as base materials, such as adhesives, a binder, and a coating.

[0003] The copolymer which consists of a cyclopentadiene and/or a dicyclopentadiene, and one or more sorts of compounds chosen from the group which consists of styrene, alpha methyl styrene, and vinyltoluene as the manufacture approach of such a copolymer is manufactured by the copolymerization reaction, subsequently is hydrogenated, and 3g/100g is exceeded, and it has the bromine number of 7g / 100g or less, and the method of manufacturing the hydrogenation object of this copolymer whose softening temperature is 50-165 degrees C is learned (refer to JP,5-66401,B).

[0004] However, as for adhesives, a binder, etc., the low melt viscosity-ization is usually demanded from the field of the workability. In order to form adhesives and the binder itself into low melt viscosity, it can attain by lowering the softening temperature of the hydrogenation resin of the copolymer of the cyclopentadiene system monomer and mono-vinyl permutation aromatic hydrocarbon which are used as the base material.

[0005] However, if the softening temperature of the above-mentioned hydrogenation resin used as a base material is lowered, the storage stability of the resin will fall. That is, when the hydrogenation resin of low softening temperature is used (for example, when softening temperature uses hydrogenation resin about 96 degrees C or less), it will block at the time of storage at the time of the storage in a warehouse etc., handling will worsen in manufacture of adhesives or a binder, and productivity will get worse.

[0006] Although the thing of high softening temperature with a natural thing will be used when [which was such] it is possible to, use the above-mentioned hydrogenation resin for the application exposed to the bottom of the elevated temperature of 50-60 degrees C, for example, the application of the binder for toners etc., on the other hand, blocking of resin became a problem in this case. For this reason, amelioration of blocking resistance is desired in hydrogenation resin.

[0007]

[Problem(s) to be Solved by the Invention] This invention solves the problem of these former and aims at offering the hydrogenation resin of the copolymer with which a hue and blocking resistance useful as a binder for toners etc. were improved as base materials, such as adhesives, a binder, and a coating.

[0008] In order to solve the above-mentioned conventional problem, as a result of repeating research wholeheartedly, when this invention persons performed the copolymerization reaction of a cyclopentadiene system monomer and the copolymer of mono-vinyl permutation aromatic

hydrocarbon, a hue came to complete this invention for the hydrogenation resin with which it was good with resin and blocking-proof was improved being obtained based on a header and this knowledge by controlling that rate of hydrogenation and considering as the bromine number of a certain fixed range.

[0009]

[Means for Solving the Problem] That is, this invention according to claim 1 consists of hydrogenation resin of the copolymer of a cyclopentadiene system unit and a mono-vinyl permutation aromatic hydrocarbon unit, and the blocking resistance copolymer hydrogenation object which has the bromine number of the range of 10-25g/100g is offered.

[0010]

[Embodiment of the Invention] Hereafter, this invention is explained. The blocking resistance copolymer hydrogenation object of this invention consists of hydrogenation resin of the copolymer of a cyclopentadiene system unit and a mono-vinyl permutation aromatic hydrocarbon unit.

[0011] Specifically, the cyclopentadiene system unit which constitutes one unit of a copolymer here is called a (**) dicyclopentadiene unit below cyclopentadiene unit and/or dicyclopentadiene unit [.] It comes out.

[0012] On the other hand, the mono-vinyl permutation aromatic hydrocarbon units which constitute another unit of a copolymer are one or more sorts of things specifically chosen from the styrene unit, the alpha-methyl-styrene unit, and the vinyltoluene unit.

[0013] The blocking resistance copolymer hydrogenation object of this invention consists of hydrogenation resin of the copolymer of the cyclopentadiene system unit and mono-vinyl permutation aromatic hydrocarbon unit like the above. Especially a desirable thing is hydrogenation resin of the copolymer of a (**) cyclopentadiene unit and a styrene unit.

[0014] The percentage of the cyclopentadiene system unit and mono-vinyl permutation aromatic hydrocarbon unit like the above in the blocking resistance copolymer hydrogenation object of this invention is [among a total of 100% of the weight of both] 20 % of the weight - 70 % of the weight of latters to 80 % of the weight - 30 % of the weight of former to 90 % of the weight - 20 % of the weight of former preferably 10 % of the weight - 80 % of the weight of latters.

[0015] Extent of the hydrogenation of the copolymer of the cyclopentadiene system unit and mono-vinyl permutation aromatic hydrocarbon unit in this invention is set up so that the bromine number (it measures based on JIS K 2605) of a final blocking resistance copolymer hydrogenation object may serve as the range of 10-25g/100g. The bromine number of a blocking resistance copolymer hydrogenation object is inferior to blocking resistance in their being 10g / less than 100g here. When 25g/100g is exceeded, a hue gets worse remarkably and it becomes impossible on the other hand, to use a binder, adhesives, etc. as a binder for toners etc., although the higher one of the bromine number of a blocking resistance copolymer hydrogenation object is desirable.

[0016] Moreover, 80-180 degrees C of softening temperatures of this blocking resistance copolymer hydrogenation object are 90-170 degrees C preferably.

[0017] Although such a blocking resistance copolymer hydrogenation object of this invention can be manufactured as follows, for example, it is not limited to this.

[0018] That is, the monomer which constitutes a cyclopentadiene system unit, and the monomer which constitutes a mono-vinyl permutation aromatic hydrocarbon unit are copolymerized, the copolymer which consists of a cyclopentadiene system unit and a mono-vinyl permutation aromatic hydrocarbon unit is manufactured, subsequently this copolymer is hydrogenated and the blocking resistance copolymer hydrogenation object which has the bromine number of the range of 10-25g/100g made into the purpose is manufactured.

[0019] As a monomer which constitutes a cyclopentadiene system unit here, a (**) cyclopentadiene is called below cyclopentadiene and/or dicyclopentadiene [.] *****. On the other hand, as a monomer which constitutes a mono-vinyl permutation aromatic hydrocarbon unit, one or more sorts of things chosen from styrene, alpha methyl styrene, and vinyltoluene are used. What made a (**) cyclopentadiene and styrene the raw material monomer especially is desirable.

[0020] The monomer which constitutes the above-mentioned cyclopentadiene system unit, and the monomer which constitutes a mono-vinyl permutation aromatic hydrocarbon unit should just set up each amount used so that the percentage of a cyclopentadiene system unit and a mono-vinyl permutation aromatic hydrocarbon unit may serve as [among a total of 100% of the weight of both] 20 % of the weight - 70 % of the weight of latters to 80 % of the weight - 30 % of the weight of former to 90 % of the weight - 20 % of the weight of former preferably 10 % of the weight - 80 % of the weight of latters.

[0021] In addition, about the reaction condition in a copolymerization reaction, 180-320 degrees C of reaction temperature are 200-300 degrees C preferably. Moreover, reaction time is 1.5 - 5 hours preferably for 1 to 8 hours. furthermore, reaction pressure -- 0-30 kg/cm² G -- 5-20kg/cm² is G preferably.

[0022] A solvent may be used on the occasion of a copolymerization reaction. As such a solvent, a xylene, toluene, kerosine, ethylcyclohexane, dimethylcyclohexane, a cyclohexane, n-octane, an isooctane, etc. can be mentioned, for example. Also in these, a xylene and toluene are suitable. a total of 100 weight sections of the raw material monomer which described the amount of the solvent used above -- receiving -- usually -- the 10 - 300 weight section -- it is the 20 - 200 weight section preferably.

[0023] What is necessary is just to carry out the polymerization of this copolymerization reaction at the temperature of 200-300 degrees C, after adding serially, applying the above-mentioned raw material monomer for 0 to 240 minutes into the solvent which could perform using the approach used for the usual polymerization reaction, for example, was heated at 200-300 degrees C (dropping).

[0024] Subsequently, the copolymer obtained by doing in this way is hydrogenated, and the blocking resistance copolymer hydrogenation object which has the hydrogenation resin of a copolymer, i.e., the bromine number of the range of 10-25g/100g made into the purpose, is manufactured.

[0025] Use of the catalyst of Pd system is suitable for this hydrogenation reaction especially using the catalyst of nickel, Co, Pd, and Ru system. Moreover, on the occasion of a reaction, solvents, such as ethylcyclohexane, dimethylcyclohexane, a cyclohexane, n-octane, and an isooctane, can be used if needed. the amount of solvents used at this time -- the above-mentioned copolymer 100 weight section -- receiving -- the 50 - 500 weight section -- it is the 50 - 400 weight section preferably.

[0026] In addition, a reaction condition is set up so that the bromine number of the above-mentioned range can be attained. The pressure at the time of reaction temperature adding 100-260 degrees C, and reaction time adding preferably 50-280 degrees C of hydrogen for 0.5 to 8 hours for 0.5 to 10 hours is 2-8MPa preferably two to 10 MPa.

[0027] The blocking resistance copolymer hydrogenation object which has the bromine number of the range of 10-25g/100g made into the purpose as mentioned above is obtained. 80-180 degrees C, softening temperature is a 90-170-degree C thing preferably, and this blocking resistance copolymer hydrogenation object excels [softening temperature] in a hue and blocking resistance, as described above.

[0028] This blocking resistance copolymer hydrogenation object can be used very effectively as a binder for toners etc. as base materials, such as adhesives and a binder. Furthermore, the blocking resistance copolymer hydrogenation object of this invention can be used as the binder for toners, can be used together with well-known binding resin (for example, a polystyrene and styrene-acrylic ester copolymer, a styrene-butadiene copolymer, polyester, etc.) (using to binding resin for example, at about 5 - 50% of the weight of a rate), and it can also be used as a constituent for toners. In this case, various assistants, such as a coloring agent and an electrification control agent, can be blended.

[0029]

[Example] Hereafter, although an example explains this invention in detail, this invention is not restricted at all by these.

[0030] The example 1 (manufacture of the copolymer A of a cyclopentadiene and styrene) of manufacture

In the 1l. (L) ***** reactor with the agitator permuted with nitrogen, xylene 154g (it is the about 30 weight section to the raw material monomer 100 weight section) was extracted as a solvent, and mixture (cyclopentadiene 269g (50% of the weight of a raw material monomer) and styrene 269g (50% of the weight of a raw material monomer)) was serially added over 2 hours to this, heating and stirring to 230 degrees C. Then, reaction mixture was made to react for 4 hours after carrying out the temperature up of the reaction mixture to 260 degrees C over 105 minutes.

[0031] Reaction generation liquid was taken out after reaction termination, it processed by the temperature of 200 degrees C, and pressure 10mmHg for 3 hours using the rotary evaporator, an unreacted monomer and an unreacted xylene were removed, and the copolymer A of a 510g cyclopentadiene and styrene was obtained. The descriptions of this copolymer A were 115 degrees C (ring and ball method) of softening temperatures, 43 % of the weight (styrene criteria) of residual styrene contents, and the bromine numbers (it measures based on JIS K 2605) 54g/100g.

[0032] The example 2 (manufacture of the hydrogenation object of the copolymer A of a cyclopentadiene and styrene) of manufacture

Copolymer A obtained in cyclohexane 75g and the example 1 of manufacture as a solvent in 300ml ***** reactor with the agitator permuted with nitrogen 75g and 4.0g of 0.5% of the weight of palladium support silica-alumina catalysts were extracted, the hydrogenation reaction was performed at hydrogen pressure force 4MPa and the temperature of 150 degrees C for 2 hours, and the hydrogenation object (hydrogenation resin) of the copolymer A of a cyclopentadiene and styrene was manufactured. The obtained hydrogenation resin was the thing of 120 degrees C (ring and ball method) of softening temperatures, 43 % of the weight (styrene criteria) of residual styrene contents, 0 % of the weight of rates of nucleus hydrogenation, the bromine numbers 14g/100g, and a hue (Gardner chromaticity) 3.

[0033] The example 3 (manufacture of the copolymer B of a cyclopentadiene and styrene) of manufacture

In the example 1 of manufacture, except having changed the polymerization reaction time after a temperature up into the temperature of 260 degrees C from 4 hours in 3 hours and 30 minutes, it carried out like the example 1 of manufacture, and the copolymer B of a 505g cyclopentadiene and styrene was obtained. The descriptions of this copolymer B were 110 degrees C (ring and ball method) of softening temperatures, 43 % of the weight (styrene criteria) of residual styrene contents, and the bromine numbers (it measures based on JIS K 2605) 54g/100g.

[0034] The example 4 (manufacture of the hydrogenation object of the copolymer B of a cyclopentadiene and styrene) of manufacture

While changing the temperature at the time of hydrogenation into 200 degrees C from 150 degrees C, using the copolymer B obtained in the example 3 of manufacture, except having changed reaction time from 2 hours in 1 hour, it carried out like the example 2 of manufacture, and the hydrogenation object (hydrogenation resin) of the copolymer B of a cyclopentadiene and styrene was manufactured. The obtained hydrogenation resin was the thing of 120 degrees C (ring and ball method) of softening temperatures, 38 % of the weight (styrene criteria) of residual styrene contents, 12 % of the weight of rates of nucleus hydrogenation, the bromine numbers 13g/100g, and a hue (Gardner chromaticity) 2.

[0035] The example 5 (manufacture of the copolymer C of a cyclopentadiene and styrene) of manufacture

In the example 1 of manufacture, except having changed the polymerization reaction time after a temperature up into the temperature of 260 degrees C from 4 hours in 3 hours and 10 minutes, it carried out like the example 1 of manufacture, and the copolymer C of a 507g cyclopentadiene and styrene was obtained. The descriptions of this copolymer C were 107 degrees C (ring and ball method) of softening temperatures, 45 % of the weight (styrene criteria) of residual styrene contents, and the bromine numbers (it measures based on JIS K 2605) 52g/100g.

[0036] The example 6 (manufacture of the hydrogenation object of the copolymer C of a cyclopentadiene and styrene) of manufacture

While changing the temperature at the time of hydrogenation into 200 degrees C from 150

degrees C, using the copolymer C obtained in the example 5 of manufacture, except having changed reaction time from 2 hours in 1 hour, it carried out like the example 2 of manufacture, and the hydrogenation object (hydrogenation resin) of the copolymer C of a cyclopentadiene and styrene was manufactured. The obtained hydrogenation resin was the thing of 122 degrees C (ring and ball method) of softening temperatures, 36 % of the weight (styrene criteria) of residual styrene contents, 20 % of the weight of rates of nucleus hydrogenation, the bromine numbers 10g/100g, and a hue (Gardner chromaticity) 1.

[0037] The example 7 (manufacture of the hydrogenation object of the copolymer A of a cyclopentadiene and styrene) of manufacture

Using the copolymer A obtained in the example 1 of manufacture, except having changed the reaction time at the time of hydrogenation in 45 minutes from 2 hours, it carried out like the example 2 of manufacture, and the hydrogenation object (hydrogenation resin) of the copolymer A of a cyclopentadiene and styrene was manufactured. The obtained hydrogenation resin was the thing of 118 degrees C (ring and ball method) of softening temperatures, 43 % of the weight (styrene criteria) of residual styrene contents, 0 % of the weight of rates of nucleus hydrogenation, the bromine numbers 25g/100g, and a hue (Gardner chromaticity) 5.

[0038] The example 1 (manufacture of the copolymer D of a cyclopentadiene and styrene) of comparison manufacture

In the example 1 of manufacture, except having changed the polymerization reaction time after a temperature up into the temperature of 260 degrees C from 4 hours in 2 hours and 50 minutes, it carried out like the example 1 of manufacture, and the copolymer D of a 500g cyclopentadiene and styrene was obtained. The descriptions of this copolymer D were 95 degrees C (ring and ball method) of softening temperatures, 45 % of the weight (styrene criteria) of residual styrene contents, and the bromine numbers (it measures based on JIS K 2605) 52g/100g.

[0039] The example 2 (manufacture of the hydrogenation object of the copolymer D of a cyclopentadiene and styrene) of comparison manufacture

While changing the temperature at the time of hydrogenation into 200 degrees C from 150 degrees C, using the copolymer D obtained in the example 1 of comparison manufacture, except having changed reaction time from 2 hours in 1 hour, it carried out like the example 2 of manufacture, and the hydrogenation object (hydrogenation resin) of the copolymer D of a cyclopentadiene and styrene was manufactured. The obtained hydrogenation resin was 120 degrees C (ring and ball method) of softening temperatures, 23 % of the weight (styrene criteria) of residual styrene contents, 51 % of the weight of rates of nucleus hydrogenation, the bromine numbers 5g/100g, and an one or less hue (Gardner chromaticity) thing.

[0040] The example 3 (manufacture of the hydrogenation object of the copolymer A of a cyclopentadiene and styrene) of comparison manufacture

Except having changed the reaction time at the time of hydrogenation in 30 minutes from 2 hours, it carried out like the example 2 of manufacture, and the hydrogenation object (hydrogenation resin) of the copolymer A of a cyclopentadiene and styrene was manufactured. The obtained hydrogenation resin was the thing of 120 degrees C (ring and ball method) of softening temperatures, 43 % of the weight (styrene criteria) of residual styrene contents, 0 % of the weight of rates of nucleus hydrogenation, the bromine numbers 30g/100g, and a hue (Gardner chromaticity) 7.

[0041] Blocking nature was evaluated by the following approach, respectively about the hydrogenation object (hydrogenation resin) of the copolymer of a cyclopentadiene and styrene obtained in examples 1-4 and the example 1 of a comparison - the examples 2, 4, 6, and 7 of 2 manufactures, and the examples 2 and 3 of comparison manufacture. A result is shown in the 1st table.

[0042] Each hydrogenation resin was put into the hot melt type adhesives applicator (180-degree-C type), and from the nozzle point, this resin was sent small quantity every and it considered as the pellet of the shape of a semi-sphere with a diameter of about 4mm. what put each pellet 10g into the plastic bag with a magnitude of 4x4.5cm -- 60 g/cm2 a load -- equal -- starting -- making -- constant temperature -- it put into the constant humidity chamber (temperature: 60 degrees C, 30% of humidity). 10 hours after, each sample was taken out,

weighing capacity of the weight of the blocked resin was carried out, and the rate of blocking was calculated by the degree type. Moreover, the condition of the blocked resin was observed visually.

[0043]

[Equation 1] Rate of blocking [weight [of the blocked resin] (g) / 10] (g) x100 [0044]

[Table 1]

第1表

	実施例 1	実施例 2	実施例 3	実施例 4	比較例 1	比較例 2
使用水添樹脂	製造例 2	製造例 4	製造例 6	製造例 7	比較製造例 2	比較製造例 3
軟化点 (°C)	120	120	122	118	120	120
臭素価(g/100g)	14	13	10	25	5	30
核水添率	0 %	12 %	20 %	0 %	51 %	0 %
色相 (ガードナー色度)	3	2	1	5	1 以下	7
ブロッキング率	0 %	0 %	2 %	0 %	20 %	0 %
ブロッキングした樹脂の状態	—	—	手で触ると、軽くほぐれた	—	固くブロッキングしていた	—

[0045] According to the 1st table, when the bromine number of the hydrogenation object (hydrogenation resin) of the copolymer of a cyclopentadiene and styrene is too high, it understands [that a hue gets worse or]. Moreover, conversely, when the bromine number is too low, it turns out that resin causes blocking.

[0046]

[Effect of the Invention] The hydrogenation resin of this invention has a good hue. And as for the hydrogenation resin of this invention, blocking-proof is improved. Therefore, among the hydrogenation resin of this invention, storage stability [/ in a warehouse etc.] becomes good, and the thing of low softening temperature serves as a very useful base material in manufacture of a binder, adhesives, a coating, etc.

[0047] Moreover, among the hydrogenation resin of this invention, since it does not block under an elevated temperature, the thing of high softening temperature can be used as a binder for toners used under an elevated temperature. Furthermore, the blocking resistance copolymer hydrogenation object of this invention can be used as the binder for toners, can be used together with binding resin, and it can also be used as a constituent for toners.

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TECHNICAL FIELD

[Field of the Invention] This invention is excellent in blocking resistance, and relates to a blocking resistance copolymer hydrogenation object useful as a binder for toners etc. as base materials, such as adhesives, a binder, and a coating.

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PRIOR ART

[Description of the Prior Art] The hydrogenation resin of a cyclopentadiene system monomer and the copolymer of mono-vinyl permutation aromatic hydrocarbon is known, and it is useful as base materials, such as adhesives, a binder, and a coating.

[0003] The copolymer which consists of a cyclopentadiene and/or a dicyclopentadiene, and one or more sorts of compounds chosen from the group which consists of styrene, alpha methyl styrene, and vinyltoluene as the manufacture approach of such a copolymer is manufactured by the copolymerization reaction, subsequently is hydrogenated, and 3g/100g is exceeded, and it has the bromine number of 7g / 100g or less, and the method of manufacturing the hydrogenation object of this copolymer whose softening temperature is 50-165 degrees C is learned (refer to JP,5-66401,B).

[0004] However, as for adhesives, a binder, etc., the low melt viscosity-ization is usually demanded from the field of the workability. In order to form adhesives and the binder itself into low melt viscosity, it can attain by lowering the softening temperature of the hydrogenation resin of the copolymer of the cyclopentadiene system monomer and mono-vinyl permutation aromatic hydrocarbon which are used as the base material.

[0005] However, if the softening temperature of the above-mentioned hydrogenation resin used as a base material is lowered, the storage stability of the resin will fall. That is, when the hydrogenation resin of low softening temperature is used (for example, when softening temperature uses hydrogenation resin about 96 degrees C or less), it will block at the time of - storage at the time of the storage in a warehouse etc., handling will worsen in manufacture of adhesives or a binder, and productivity will get worse.

[0006] Although the thing of high softening temperature with a natural thing will be used when [which was such] it is possible to, use the above-mentioned hydrogenation resin for the application exposed to the bottom of the elevated temperature of 50-60 degrees C, for example, the application of the binder for toners etc., on the other hand, blocking of resin became a problem in this case. For this reason, amelioration of blocking resistance is desired in hydrogenation resin.

[0007]

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EFFECT OF THE INVENTION

[Effect of the Invention] The hydrogenation resin of this invention has a good hue. And as for the hydrogenation resin of this invention, blocking-proof is improved. Therefore, among the hydrogenation resin of this invention, storage stability [/ in a warehouse etc.] becomes good, and the thing of low softening temperature serves as a very useful base material in manufacture of a binder, adhesives, a coating, etc.

[0047] Moreover, among the hydrogenation resin of this invention, since it does not block under an elevated temperature, the thing of high softening temperature can be used as a binder for toners used under an elevated temperature. Furthermore, the blocking resistance copolymer hydrogenation object of this invention can be used as the binder for toners, can be used together with binding resin, and it can also be used as a constituent for toners.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention solves the problem of these former and aims at offering the hydrogenation resin of the copolymer with which a hue and blocking resistance useful as a binder for toners etc. were improved as base materials, such as adhesives, a binder, and a coating.

[0008] In order to solve the above-mentioned conventional problem, as a result of repeating research wholeheartedly, when this invention persons performed the copolymerization reaction of a cyclopentadiene system monomer and the copolymer of mono-vinyl permutation aromatic hydrocarbon, a hue came to complete this invention for the hydrogenation resin with which it was good with resin and blocking-proof was improved being obtained based on a header and this knowledge by controlling that rate of hydrogenation and considering as the bromine number of a certain fixed range.

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MEANS

[Means for Solving the Problem] That is, this invention according to claim 1 consists of hydrogenation resin of the copolymer of a cyclopentadiene system unit and a mono-vinyl permutation aromatic hydrocarbon unit, and the blocking resistance copolymer hydrogenation object which has the bromine number of the range of 10-25g/100g is offered.

[0010]

[Embodiment of the Invention] Hereafter, this invention is explained. The blocking resistance copolymer hydrogenation object of this invention consists of hydrogenation resin of the copolymer of a cyclopentadiene system unit and a mono-vinyl permutation aromatic hydrocarbon unit.

[0011] Specifically, the cyclopentadiene system unit which constitutes one unit of a copolymer here is called a (**) dicyclopentadiene unit below cyclopentadiene unit and/or dicyclopentadiene unit [.] It comes out.

[0012] On the other hand, the mono-vinyl permutation aromatic hydrocarbon units which constitute another unit of a copolymer are one or more sorts of things specifically chosen from the styrene unit, the alpha-methyl-styrene unit, and the vinyltoluene unit.

[0013] The blocking resistance copolymer hydrogenation object of this invention consists of hydrogenation resin of the copolymer of the cyclopentadiene system unit and mono-vinyl permutation aromatic hydrocarbon unit like the above. Especially a desirable thing is hydrogenation resin of the copolymer of a (**) cyclopentadiene unit and a styrene unit.

[0014] The percentage of the cyclopentadiene system unit and mono-vinyl permutation aromatic hydrocarbon unit like the above in the blocking resistance copolymer hydrogenation object of this invention is [among a total of 100% of the weight of both] 20 % of the weight - 70 % of the weight of latters to 80 % of the weight - 30 % of the weight of former to 90 % of the weight - 20 % of the weight of former preferably 10 % of the weight - 80 % of the weight of latters.

[0015] Extent of the hydrogenation of the copolymer of the cyclopentadiene system unit and mono-vinyl permutation aromatic hydrocarbon unit in this invention is set up so that the bromine number (it measures based on JIS K 2605) of a final blocking resistance copolymer hydrogenation object may serve as the range of 10-25g/100g. The bromine number of a blocking resistance copolymer hydrogenation object is inferior to blocking resistance in their being 10g / less than 100g here. When 25g/100g is exceeded, a hue gets worse remarkably and it becomes impossible on the other hand, to use a binder, adhesives, etc. as a binder for toners etc., although the higher one of the bromine number of a blocking resistance copolymer hydrogenation object is desirable.

[0016] Moreover, 80-180 degrees C of softening temperatures of this blocking resistance copolymer hydrogenation object are 90-170 degrees C preferably.

[0017] Although such a blocking resistance copolymer hydrogenation object of this invention can be manufactured as follows, for example, it is not limited to this.

[0018] That is, the monomer which constitutes a cyclopentadiene system unit, and the monomer which constitutes a mono-vinyl permutation aromatic hydrocarbon unit are copolymerized, the copolymer which consists of a cyclopentadiene system unit and a mono-vinyl permutation aromatic hydrocarbon unit is manufactured, subsequently this copolymer is hydrogenated and

the blocking resistance copolymer hydrogenation object which has the bromine number of the range of 10-25g/100g made into the purpose is manufactured.

[0019] As a monomer which constitutes a cyclopentadiene system unit here, a (**)
cyclopentadiene is called below cyclopentadiene and/or dicyclopentadiene [.] *****. On the other hand, as a monomer which constitutes a mono-vinyl permutation aromatic hydrocarbon unit, one or more sorts of things chosen from styrene, alpha methyl styrene, and vinyltoluene are used. What made a (**) cyclopentadiene and styrene the raw material monomer especially is desirable.

[0020] The monomer which constitutes the above-mentioned cyclopentadiene system unit, and the monomer which constitutes a mono-vinyl permutation aromatic hydrocarbon unit should just set up each amount used so that the percentage of a cyclopentadiene system unit and a mono-vinyl permutation aromatic hydrocarbon unit may serve as [among a total of 100% of the weight of both] 20 % of the weight - 70 % of the weight of latters to 80 % of the weight - 30 % of the weight of former to 90 % of the weight - 20 % of the weight of former preferably 10 % of the weight - 80 % of the weight of latters.

[0021] In addition, about the reaction condition in a copolymerization reaction, 180-320 degrees C of reaction temperature are 200-300 degrees C preferably. Moreover, reaction time is 1.5 - 5 hours preferably for 1 to 8 hours. furthermore, reaction pressure -- 0-30 kg/cm2 G -- 5-20kg/cm2 is G preferably.

[0022] A solvent may be used on the occasion of a copolymerization reaction. As such a solvent, a xylene, toluene, kerosine, ethylcyclohexane, dimethylcyclohexane, a cyclohexane, n-octane, an isooctane, etc. can be mentioned, for example. Also in these, a xylene and toluene are suitable. a total of 100 weight sections of the raw material monomer which described the amount of the solvent used above -- receiving -- usually -- the 10 - 300 weight section -- it is the 20 - 200 weight section preferably.

[0023] What is necessary is just to carry out the polymerization of this copolymerization reaction at the temperature of 200-300 degrees C, after adding serially, applying the above-mentioned raw material monomer for 0 to 240 minutes into the solvent which could perform using the approach used for the usual polymerization reaction, for example, was heated at 200-300 degrees C (dropping).

[0024] Subsequently, the copolymer obtained by doing in this way is hydrogenated, and the blocking resistance copolymer hydrogenation object which has the hydrogenation resin of a copolymer, i.e., the bromine number of the range of 10-25g/100g made into the purpose, is manufactured.

[0025] Use of the catalyst of Pd system is suitable for this hydrogenation reaction especially using the catalyst of nickel, Co, Pd, and Ru system. Moreover, on the occasion of a reaction, solvents, such as ethylcyclohexane, dimethylcyclohexane, a cyclohexane, n-octane, and an isooctane, can be used if needed. the amount of solvents used at this time -- the above-mentioned copolymer 100 weight section -- receiving -- the 50 - 500 weight section -- it is the 50 - 400 weight section preferably.

[0026] In addition, a reaction condition is set up so that the bromine number of the above-mentioned range can be attained. The pressure at the time of reaction temperature adding 100-260 degrees C, and reaction time adding preferably 50-280 degrees C of hydrogen for 0.5 to 8 hours for 0.5 to 10 hours is 2-8MPa preferably two to 10 MPa.

[0027] The blocking resistance copolymer hydrogenation object which has the bromine number of the range of 10-25g/100g made into the purpose as mentioned above is obtained. 80-180 degrees C, softening temperature is a 90-170-degree C thing preferably, and this blocking resistance copolymer hydrogenation object excels [softening temperature] in a hue and blocking resistance, as described above.

[0028] This blocking resistance copolymer hydrogenation object can be used very effectively as a binder for toners etc. as base materials, such as adhesives and a binder. Furthermore, the blocking resistance copolymer hydrogenation object of this invention can be used as the binder for toners, can be used together with well-known binding resin (for example, a polystyrene and styrene-acrylic ester copolymer, a styrene-butadiene copolymer, polyester, etc.) (using to

binding resin for example, at about 5 – 50% of the weight of a rate), and it can also be used as a constituent for toners. In this case, various assistants, such as a coloring agent and an electrification control agent, can be blended.

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EXAMPLE

[Example] Hereafter, although an example explains this invention in detail, this invention is not restricted at all by these.

[0030] The example 1 (manufacture of the copolymer A of a cyclopentadiene and styrene) of manufacture

In the 1l. (L) ***** reactor with the agitator permuted with nitrogen, xylene 154g (it is the about 30 weight section to the raw material monomer 100 weight section) was extracted as a solvent, and mixture (cyclopentadiene 269g (50% of the weight of a raw material monomer) and styrene 269g (50% of the weight of a raw material monomer)) was serially added over 2 hours to this, heating and stirring to 230 degrees C. Then, reaction mixture was made to react for 4 hours after carrying out the temperature up of the reaction mixture to 260 degrees C over 105 minutes.

[0031] Reaction generation liquid was taken out after reaction termination, it processed by the temperature of 200 degrees C, and pressure 10mmHg for 3 hours using the rotary evaporator, an unreacted monomer and an unreacted xylene were removed, and the copolymer A of a 510g cyclopentadiene and styrene was obtained. The descriptions of this copolymer A were 115 degrees C (ring and ball method) of softening temperatures, 43 % of the weight (styrene criteria) of residual styrene contents, and the bromine numbers (it measures based on JIS K 2605) 54g/100g.

[0032] The example 2 (manufacture of the hydrogenation object of the copolymer A of a cyclopentadiene and styrene) of manufacture

Copolymer A obtained in cyclohexane 75g and the example 1 of manufacture as a solvent in 300ml ***** reactor with the agitator permuted with nitrogen 75g and 4.0g of 0.5% of the weight of palladium support silica-alumina catalysts were extracted, the hydrogenation reaction was performed at hydrogen pressure force 4MPa and the temperature of 150 degrees C for 2 hours, and the hydrogenation object (hydrogenation resin) of the copolymer A of a cyclopentadiene and styrene was manufactured. The obtained hydrogenation resin was the thing of 120 degrees C (ring and ball method) of softening temperatures, 43 % of the weight (styrene criteria) of residual styrene contents, 0 % of the weight of rates of nucleus hydrogenation, the bromine numbers 14g/100g, and a hue (Gardner chromaticity) 3.

[0033] The example 3 (manufacture of the copolymer B of a cyclopentadiene and styrene) of manufacture

In the example 1 of manufacture, except having changed the polymerization reaction time after a temperature up into the temperature of 260 degrees C from 4 hours in 3 hours and 30 minutes, it carried out like the example 1 of manufacture, and the copolymer B of a 505g cyclopentadiene and styrene was obtained. The descriptions of this copolymer B were 110 degrees C (ring and ball method) of softening temperatures, 43 % of the weight (styrene criteria) of residual styrene contents, and the bromine numbers (it measures based on JIS K 2605) 54g/100g.

[0034] The example 4 (manufacture of the hydrogenation object of the copolymer B of a cyclopentadiene and styrene) of manufacture

While changing the temperature at the time of hydrogenation into 200 degrees C from 150 degrees C, using the copolymer B obtained in the example 3 of manufacture, except having

changed reaction time from 2 hours in 1 hour, it carried out like the example 2 of manufacture, and the hydrogenation object (hydrogenation resin) of the copolymer B of a cyclopentadiene and styrene was manufactured. The obtained hydrogenation resin was the thing of 120 degrees C (ring and ball method) of softening temperatures, 38 % of the weight (styrene criteria) of residual styrene contents, 12 % of the weight of rates of nucleus hydrogenation, the bromine numbers 13g/100g, and a hue (Gardner chromaticity) 2.

[0035] The example 5 (manufacture of the copolymer C of a cyclopentadiene and styrene) of manufacture

In the example 1 of manufacture, except having changed the polymerization reaction time after a temperature up into the temperature of 260 degrees C from 4 hours in 3 hours and 10 minutes, it carried out like the example 1 of manufacture, and the copolymer C of a 507g cyclopentadiene and styrene was obtained. The descriptions of this copolymer C were 107 degrees C (ring and ball method) of softening temperatures, 45 % of the weight (styrene criteria) of residual styrene contents, and the bromine numbers (it measures based on JIS K 2605) 52g/100g.

[0036] The example 6 (manufacture of the hydrogenation object of the copolymer C of a cyclopentadiene and styrene) of manufacture

While changing the temperature at the time of hydrogenation into 200 degrees C from 150 degrees C, using the copolymer C obtained in the example 5 of manufacture, except having changed reaction time from 2 hours in 1 hour, it carried out like the example 2 of manufacture, and the hydrogenation object (hydrogenation resin) of the copolymer C of a cyclopentadiene and styrene was manufactured. The obtained hydrogenation resin was the thing of 122 degrees C (ring and ball method) of softening temperatures, 36 % of the weight (styrene criteria) of residual styrene contents, 20 % of the weight of rates of nucleus hydrogenation, the bromine numbers 10g/100g, and a hue (Gardner chromaticity) 1.

[0037] The example 7 (manufacture of the hydrogenation object of the copolymer A of a cyclopentadiene and styrene) of manufacture

Using the copolymer A obtained in the example 1 of manufacture, except having changed the reaction time at the time of hydrogenation in 45 minutes from 2 hours, it carried out like the example 2 of manufacture, and the hydrogenation object (hydrogenation resin) of the copolymer A of a cyclopentadiene and styrene was manufactured. The obtained hydrogenation resin was the thing of 118 degrees C (ring and ball method) of softening temperatures, 43 % of the weight (styrene criteria) of residual styrene contents, 0 % of the weight of rates of nucleus hydrogenation, the bromine numbers 25g/100g, and a hue (Gardner chromaticity) 5.

[0038] The example 1 (manufacture of the copolymer D of a cyclopentadiene and styrene) of comparison manufacture

In the example 1 of manufacture, except having changed the polymerization reaction time after a temperature up into the temperature of 260 degrees C from 4 hours in 2 hours and 50 minutes, it carried out like the example 1 of manufacture, and the copolymer D of a 500g cyclopentadiene and styrene was obtained. The descriptions of this copolymer D were 95 degrees C (ring and ball method) of softening temperatures, 45 % of the weight (styrene criteria) of residual styrene contents, and the bromine numbers (it measures based on JIS K 2605) 52g/100g.

[0039] The example 2 (manufacture of the hydrogenation object of the copolymer D of a cyclopentadiene and styrene) of comparison manufacture

While changing the temperature at the time of hydrogenation into 200 degrees C from 150 degrees C, using the copolymer D obtained in the example 1 of comparison manufacture, except having changed reaction time from 2 hours in 1 hour, it carried out like the example 2 of manufacture, and the hydrogenation object (hydrogenation resin) of the copolymer D of a cyclopentadiene and styrene was manufactured. The obtained hydrogenation resin was 120 degrees C (ring and ball method) of softening temperatures, 23 % of the weight (styrene criteria) of residual styrene contents, 51 % of the weight of rates of nucleus hydrogenation, the bromine numbers 5g/100g, and an one or less hue (Gardner chromaticity) thing.

[0040] The example 3 (manufacture of the hydrogenation object of the copolymer A of a cyclopentadiene and styrene) of comparison manufacture

Except having changed the reaction time at the time of hydrogenation in 30 minutes from 2

hours, it carried out like the example 2 of manufacture, and the hydrogenation object (hydrogenation resin) of the copolymer A of a cyclopentadiene and styrene was manufactured. The obtained hydrogenation resin was the thing of 120 degrees C (ring and ball method) of softening temperatures, 43 % of the weight (styrene criteria) of residual styrene contents, 0 % of the weight of rates of nucleus hydrogenation, the bromine numbers 30g/100g, and a hue (Gardner chromaticity) 7.

[0041] Blocking nature was evaluated by the following approach, respectively about the hydrogenation object (hydrogenation resin) of the copolymer of a cyclopentadiene and styrene obtained in examples 1-4 and the example 1 of a comparison - the examples 2, 4, 6, and 7 of 2 manufactures, and the examples 2 and 3 of comparison manufacture. A result is shown in the 1st table.

[0042] Each hydrogenation resin was put into the hot melt type adhesives applicator (180-degree-C type), and from the nozzle point, this resin was sent small quantity every and it considered as the pellet of the shape of a semi-sphere with a diameter of about 4mm. what put each pellet 10g into the plastic bag with a magnitude of 4x4.5cm -- 60 g/cm2 a load -- equal -- starting -- making -- constant temperature -- it put into the constant humidity chamber (temperature: 60 degrees C, 30% of humidity). 10 hours after, each sample was taken out, weighing capacity of the weight of the blocked resin was carried out, and the rate of blocking was calculated by the degree type. Moreover, the condition of the blocked resin was observed visually.

[0043]

[Equation 1] Rate = of blocking [weight [of the blocked resin] (g) / 10] (g) x100 [0044]

[Table 1]

第1表

	実施例1	実施例2	実施例3	実施例4	比較例1	比較例2
使用水添樹脂	製造例2	製造例4	製造例6	製造例7	比較製造例2	比較製造例3
軟化点 (°C)	120	120	122	118	120	120
臭素価(g/100g)	14	13	10	25	5	30
核水添率	0 %	12 %	20 %	0 %	51 %	0 %
色相 (ガードナー色度)	3	2	1	5	1以下	7
ブロッキング率	0 %	0 %	2 %	0 %	20 %	0 %
ブロッキングした樹脂の状態	—	—	手で触ると、軽くほぐれた	—	固くブロッキングしていた	—

[0045] According to the 1st table, when the bromine number of the hydrogenation object (hydrogenation resin) of the copolymer of a cyclopentadiene and styrene is too high, it understands [that a hue gets worse or]. Moreover, conversely, when the bromine number is too low, it turns out that resin causes blocking.

[Translation done.]

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